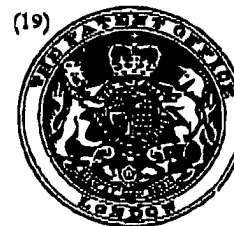


## PATENT SPECIFICATION

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## (54) FUSED OXIDE GLASSES

(71) We, CORNING GLASS WORKS, a corporation organised under the laws of the State of New York, United States of America of Corning, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fused oxide glasses, in particular to such glasses when produced by the flame hydrolysis technique. It is more particularly concerned with such glasses comprising, at least in part, at least one of  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{TeO}_2$ , and  $\text{Sb}_2\text{O}_3$ .

The flame hydrolysis technique was originally developed as a method of producing pure silica particles. If desired, these particles might then be vitrified to form a transparent glass composed essentially of  $\text{SiO}_2$ . The technique comprises passing the vapour of a hydrolysable compound, e.g. silicon tetrachloride, into a burner flame of combustible gas to hydrolyse the vapour and decompose the hydrolysis product to form the corresponding oxide. This process is described in detail in United States Patent No. 2,272,342.

The oxide particles formed may be collected in particulate form (known as soot) and used as, e.g., fillers, extenders and pigments. They may also be pressed in a mould, or collected on a mandrel, to form a shape that can be consolidated and vitrified by further heat treatment.

It has been found, however, that a glass body can be formed directly by carrying out the collection process in a furnace maintained at a sufficiently high temperature. Normally, a glass body may be formed by directly depositing particles, in vitreous form, on a base rotated in a chamber heated to a temperature of from 1750 to 1850°C. In this way, the particles are collected as a solid body, or boule, of clear transparent glass in a single process step. The obvious advantages of such direct vitrification and collection have led to the adoption of this

technique as the standard commercial practice in the production of fused silica glasses. In particular, the process is used for the production by flame hydrolysis of large bodies or boules of fused silica and titania-doped silica.

The desirability of introducing small amounts of additive oxides into the fused silica glass (known as doping) quickly becomes apparent. Techniques based on the use of mixed vapours are described in United States Patent Nos. 2,239,551 and 2,326,059. A more recent patent, United States Patent No. 3,334,982, describes glasses produced in this manner which are stated to contain different additives including up to 0.5% germania ( $\text{GeO}_2$ ).

It is customary to calculate glass compositions on an oxide basis. In a multi-component glass, the proportions are calculated on the basis of, or corresponding to, a raw material batch from which the glass is melted. In the case of fused oxide glasses produced by the flame hydrolysis technique, the raw materials, typically, are chloride vapours. Accordingly, unless otherwise indicated, the relative proportions of oxides in a mixed oxide glass of this type are calculated in conventional manner from the relative amounts of chloride vapours fed to the burner flame.

The present invention arose from efforts made to study fused silica glasses produced by direct vitrification and containing a variety of different dopants. These glasses included, *inter alia*, fused silica glasses containing  $\text{GeO}_2$  as a dopant. Substantial quantities of germanium chloride ( $\text{GeCl}_4$ ) could be admixed with silicon tetrachloride. However, it was unexpectedly found that the resulting fused silica glass invariably contained less than 0.1% by weight,  $\text{GeO}_2$ , regardless of the amount of germanium chloride supplied to the mixture. For example, a chloride mixture, proportioned to produce a binary fused silica glass containing 7% by weight,  $\text{GeO}_2$ , actually produced a glass containing only approx-

imately 0.03% by weight,  $\text{GeO}_2$ , as determined by chemical analysis.

Subsequent studies with other additive materials, in particular  $\text{P}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{TeO}_2$ , revealed that these oxides behave in a manner similar to  $\text{GeO}_2$ . Thus, these oxides cannot be introduced into a fused silica glass in any substantial amount by the conventional procedure of direct vitrification and collection as a glass body.

It may be theorized that the combustion flame temperature, combined with the overall furnace temperature of from 1750 to 1850°C., is sufficiently high that the oxides concerned tend to volatilize rather than vitrify. Available vapour pressure data tend to support such a theory. However, such data also predict similar volatilization, at least to a substantial degree, at the lower temperatures successfully used in accordance with the present invention. In any event, it was not possible to produce the present glasses by conventional fused silica production processes.

It is, of course, known to produce binary  $\text{GeO}_2$ - $\text{SiO}_2$  glasses by the conventional batch melting procedure. For example, such glasses and the melting procedure for their production are described in United States Patent No. 3,542,572.

A particular feature of fused oxide glasses produced by flame hydrolysis is an impurity level considerably lower than that normally attainable in ordinary melted glasses. For example, fused silica glasses are produced by this process with a cation impurity level below 10 ppm, by weight. In contrast, the impurity level in even relatively pure melted glasses will be in the range of from 0.01 to 0.1% by weight, i.e. from 100 to 1,000 ppm. The term "impurity" has its normal meaning as referring to a material that is not intentionally added and generally has an adverse effect upon the desirable properties of a product. By the term "cation impurity level", is meant the amount of transition metal ions, e.g. iron, which seriously interfere with optical transmission.

It has now been discovered that fused oxide glasses containing  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{TeO}_2$ , and/or  $\text{Sb}_2\text{O}_3$ , can be produced despite the fact that the conventional process of direct vitrification and collection has proven quite impractical with respect to these oxides. More particularly, it has been found that such fused oxide glasses may be produced by depositing the oxide particles as a porous body and then consolidating this porous body to a solid non-porous body. The temperature must not exceed 1600°C., and should be maintained, during consolidation, within a range varying between the minimum consolidation temperature of a particular glass and 200 deg C. thereabove.

The present invention therefore provides

a fused oxide glass, being either a tellurate glass or a glass comprising at least one oxide selected from  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{Sb}_2\text{O}_3$ , comprising  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_3$ , or  $\text{TeO}_2$ , in an amount in excess of 0.1% by weight, and having a cation impurity level, as hereinbefore defined, not exceeding 10 ppm, by weight.

The invention also provides a method of making such a glass comprising:

(a) entraining in a gas stream at least one vaporizable compound, at least one of which may be converted, by flame hydrolysis and decomposition, into  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{TeO}_2$ , or  $\text{Sb}_2\text{O}_3$ , in an amount in excess of 0.1% by weight;

(b) passing the gas stream into the flame of a combustion burner;

(c) collecting the resulting oxide in particulate form;

(d) shaping the oxide particles as a porous body;

(e) heating the said shaped body to consolidate the porous body to a non-porous glass body; and

(f) maintaining the particle temperature at not more than 1600°C., and at not more than 200 deg C above the minimum consolidation temperature of the porous body, during the deposition and consolidation steps.

The simplest form of the present invention is a glass composed entirely of one of the indicated oxides, other than  $\text{TeO}_2$ . Such glass may be produced from any vaporizable compound that hydrolyses and converts to the oxide in a combustion burner flame. Normally, the chloride is employed because of ready availability, convenience and cost. However, other suitable compounds will be readily apparent to one skilled in the art. A compatible carrier gas is passed through a container of the chloride, or other selected vaporizable compound, to entrain the compound in vapour form and carry it to the combustion burner. The gas-vapour mixture is passed into the burner and through the burner flame to be hydrolysed and decomposed to the corresponding oxide.

The present manufacturing practice, wherein the oxide particles are deposited to produce a transparent glass body directly, is quite impractical for the present glasses. It is possible, by close temperature control, to collect a small amount of an oxide in vitreous form, but the amount lost is too large for such procedure to be practical. Furthermore, any attempt at composition control in a mixture is extremely difficult.

Instead, the oxide must be collected in particulate form as a porous body composed of densely-packed, vitreous particles. This may be accomplished in a heated chamber, providing that consolidation of the particles, as formed and deposited, is avoided. However, the particles may also be collected at room or ambient temperature and this is gen-

erally preferable for obvious reasons.

The particulate, porous body thus formed is now consolidated to a non-porous, body of corresponding shape, but smaller size by heat treatment. In accordance with the present invention, the temperature of such treatment must not exceed 1600°C. Furthermore, it should not exceed the temperature range extending 200 deg C. above the minimum consolidation temperature for the glass. The latter is the minimum temperature at which a body composed of oxide particles can be consolidated to a non-porous body within a period of one hour.

The temperature limitation is particularly important in producing single oxide glasses in accordance with the invention since there is not interaction or bonding that prevents oxide loss. Accordingly, the oxide simply fails to deposit and is lost at higher temperatures.

Practice of this embodiment of the invention is particularly described with reference to production of a pure  $\text{GeO}_2$  glass.

A stream of dry nitrogen, acting as a carrier gas, was bubbled through a constant level tank containing liquid  $\text{GeCl}_4$  at the rate of 1200 cc./min.; the  $\text{GeCl}_4$  being maintained at a temperature of 45°C. This  $\text{N}_2$ - $\text{GeCl}_4$  mixture was passed through a combustion burner wherein a blend of natural gas and oxygen was provided from a stream of natural gas flowing at 4800 cc./min. and a stream of oxygen also flowing at 4800 cc./min.

A 100%  $\text{GeO}_2$  glass, fabricated into a rod, 5 inches in length and 5 mm. in diameter, through conventional glass melting and re-drawing practice, was positioned approximately 5½ inches from the face of the burner as a bait or support for the deposit of  $\text{GeO}_2$  particles or soot. Such a glass rod was utilized to avoid extensive mismatch in thermal expansion coefficient with the soot being deposited. The bait was mounted in a manner to permit rotation and translatory movement thereof. During deposition of the oxide particles, the  $\text{GeO}_2$  glass rod was rotated at 60 rpm and translated in a reciprocatory motion under the burner at a rate of 12 inches/min. After two hours, a relatively dense, porous body of particulate  $\text{GeO}_2$  was produced having a diameter of approximately two inches.

The gas streams to the burner were then stopped and the coated support introduced longitudinally into an electric furnace operating at 950°C. and containing a helium atmosphere therein. The rate at which the composite body was introduced into the furnace was 1/4 inch/min. to ensure sound progressive consolidation. The final sintered body had a diameter of approximately 1 inch and appeared to be optically clear with essentially no gaseous inclusions.

The present invention also relates to glasses in binary systems wherein two of the indi-

cated oxides are mixed together. For example, glasses in the binary systems  $\text{GeO}_2$ - $\text{Sb}_2\text{O}_3$  and  $\text{GeO}_2$ - $\text{P}_2\text{O}_5$  can now be made using this technique. These may be produced by entraining vapours of suitable vaporizable compounds and forming a properly proportioned mixture of such vapours. This combined stream is introduced to the combustion burner where the vapours are hydrolysed and decomposed to the corresponding oxides. For example, glasses in the  $\text{GeO}_2$ - $\text{Sb}_2\text{O}_3$  system may be produced by mixing vapours of germanium chloride ( $\text{GeCl}_4$ ) and antimony chloride ( $\text{SbCl}_3$ ) in desired proportions and passing the gas stream containing such mixed vapours through a suitable combustion burner flame in the manner described above. Again the particles are collected as a porous body and this is consolidated at a temperature that should not exceed 200 deg C. above the minimum sintering temperature for the given glass.

Perhaps the most significant feature of the invention, however, is the provision of binary glass systems wherein one of the oxides used according to the present invention is mixed with a second oxide which is not of a volatile nature. Of particular interest is the binary system  $\text{GeO}_2$ - $\text{SiO}_2$ . In producing these glasses, the vapour of a suitable compound, such as  $\text{GeCl}_4$ , is mixed in calculated proportions with the vapour, or other suitable source, of a second oxide, such as  $\text{SiCl}_4$ . This mixture is then introduced into the flame of a combustion burner, in accordance with known procedures, to produce the desired oxide mixture.

This embodiment of the invention is hereafter described in terms of a silica glass system, more particularly the  $\text{GeO}_2$ - $\text{SiO}_2$  system. However, it will be appreciated that it also includes other binary glass systems and further extends to ternary and other multi-oxide glass systems. The limiting criteria are that the glass which is produced by the flame hydrolysis technique, contains not more than 10 ppm cation impurities, includes at least one oxide selected from  $\text{GeO}_2$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{TeO}_2$  and  $\text{P}_2\text{O}_5$ , and also includes at least one additional oxide. The additional oxide must, of course, be compatible, in the sense of forming a glass, with the selected oxide. Within this limitation, it may be any oxide capable of being produced by the flame hydrolysis procedure. These include  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{Nb}_2\text{O}_5$ , as well as the various oxides disclosed in U.S. Patent No. 3,801,294.

According to the present invention, it is desirable to consolidate the porous body by gradually passing the body through a zone or line of maximum temperature. In this manner, the body is gradually consolidated from one extremity to another with gases in the pores progressively being forced out of the body and not trapped therein. This

ensures a clear, transparent body without physical defects that might interfere with smooth light transmission.

The invention is further illustrated with reference to specific embodiments thereof and with reference to the accompanying drawings wherein:

FIGURES 1 and 3 are graphical illustrations showing the relationship between refractive index and oxide proportions in certain binary glass systems, and

FIGURE 2 is a graphical illustration showing the relationship between the minimum sintering temperature and oxide proportions in the  $\text{GeO}_2$ - $\text{SiO}_2$  system.

Fused oxide glasses in the  $\text{GeO}_2$ - $\text{SiO}_2$  binary system are of particular interest because of the relatively rapid rate at which the refractive index of the glass increases with increased proportion of  $\text{GeO}_2$  to  $\text{SiO}_2$  in the glass composition. This is of particular interest in the production of fibre optic elements in which glasses of differing refractive indices are combined to achieve the desired light transfer in known manner. At the same time, it is highly desirable to use glasses of similar chemical composition and having similar physical properties, as well as extremely high chemical purity.

Heretofore, glasses in the  $\text{TiO}_2$ - $\text{SiO}_2$  system have been employed. However, as described in United Kingdom Patent No. 1,213,603, these have not been entirely satisfactory because of the instability of the titanium ion valence state. The  $\text{GeO}_2$ - $\text{SiO}_2$  system glasses avoid this type of instability.

FIGURE 1 of the drawings is a graphical illustration wherein the weight percent of  $\text{GeO}_2$  in  $\text{GeO}_2$ - $\text{SiO}_2$  glasses is plotted along the horizontal axis. Thus, the horizontal axis depicts glasses varying in composition from pure  $\text{SiO}_2$  at the left-hand side of the graph to pure  $\text{GeO}_2$  at the right-hand side of the graph. The refractive index at the wavelength of the sodium D line ( $n_D$ ) is plotted along the vertical axis of the graph. Specific glass compositions which were produced, and upon which actual refractive index measurements were made, are indicated by small circles on the graph.

FIGURE 2 of the drawings is a graphical illustration in which glass compositions in the  $\text{GeO}_2$ - $\text{SiO}_2$  system are plotted along the horizontal axis in the same manner as in FIGURE 1. In FIGURE 2 the minimum consolidation temperatures for the  $\text{GeO}_2$ - $\text{SiO}_2$  glasses are plotted on the vertical axis. In accordance with preceding description, this graph shows the minimum temperature at which a porous preform body of indicated composition can be heat treated to convert it to a clear transparent glass body of corresponding shape within a period of one hour. It will be observed that these temperatures vary from approximately 900°C. for pure

$\text{GeO}_2$  to approximately 1400°C. for pure  $\text{SiO}_2$ , all temperatures being substantially below 1600°C. which is considered critical to avoid substantial loss of  $\text{GeO}_2$ . Again, circles on the graph indicate actual temperature determinations made for specific glasses having the indicated compositions.

It will be understood that the 1600°C. maximum consolidation temperature does not imply that all glasses can be successfully consolidated at or near this temperature. Thus, glasses having a minimum consolidation temperature in the range of from 900 to 1100°C., as indicated in FIGURE 2, should generally not be subjected to substantially higher temperatures than from 1100 to 1300°C. At higher temperatures, there is a tendency for the glass to slump or lose shape as well as undergo material loss by volatilisation.

The production of glasses, such as referred to in FIGURES 1 and 2, is illustrated by reference to a specific glass composed of 10% by weight,  $\text{GeO}_2$ , and 90% by weight,  $\text{SiO}_2$ .

A stream of dry nitrogen was bubbled at a rate of 3600cc./min. through a constant level tank containing a mixture of  $\text{GeCl}_4$  and  $\text{SiCl}_4$  liquids maintained at a temperature of 35°C. The liquid chloride mixture was in the proportion of 24.6% by weight,  $\text{GeCl}_4$  to 75.4% by weight,  $\text{SiCl}_4$ . The nitrogen stream passing through the chloride mixture entrained a mixture of vapours having a composition of 11% by weight,  $\text{GeCl}_4$ , and 89% by weight,  $\text{SiCl}_4$ . The mixture thus produced was piped to a combustion burner and passed through such a burner into the flame of a natural gas-oxygen mixture fed to the burner. The chloride vapours were hydrolysed and decomposed in the flame to form a  $\text{GeO}_2$ - $\text{SiO}_2$  soot, or oxide particle mixture, having a composition of approximately 11% by weight,  $\text{GeO}_2$ , and 89% by weight,  $\text{SiO}_2$ .

A fused silica rod, 5 inches in length and 5mm in diameter, was positioned 7 inches from the face of the burner as a support upon which the oxide, or soot, particles were deposited from the flame. This fused silica support was mounted in a suitable holder so that it was rotated at 60 rpm. and, at the same time, translated back and forth under the burner at a rate of 12 inches per minute. In this manner, a uniform deposition of soot took place over the surface of the support rod. The soot was deposited for a period of two hours to form a dense, porous body approximately 2 inches in diameter and 5 inches in length.

The oxide deposition was then discontinued, the body removed and introduced into an electric furnace at a rate of 1/4 inch per minute. The furnace, with a helium atmosphere, was maintained at a maximum temperature of 1400°C. and the body was progressively consolidated as it was intro-

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duced into the furnace. The result was a clear, high quality glass substantially free from gaseous inclusions and having a diameter of approximately 1 inch and a length of approximately 5 inches. Chemical analysis showed the glass to have a composition of 10% by weight,  $\text{GeO}_2$ , and 90% by weight,  $\text{SiO}_2$ .

A fused silica support was employed for collection of the oxide particles because of its low expansion coefficient. Such material is customarily used in collecting oxide soot for glasses containing up to 20% by weight,  $\text{GeO}_2$ . In the case of larger amounts of  $\text{GeO}_2$ , being present, the glass expansion increases sufficiently so that it is preferably to employ a graphite or mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) supporting member. With still larger proportions of  $\text{GeO}_2$ , particularly above 80% by weight, of this oxide, it is desirable to employ an alumina support rod or other body. It may be noted that the thermal expansion coefficient, (25–300°C), of fused germania glass, that is a glass composed entirely of  $\text{GeO}_2$ , is  $88 \times 10^{-7}/\text{deg C}$ , whereas the 10%  $\text{GeO}_2$  glass of the example has a thermal expansion coefficient (25–300°C) of  $10 \times 10^{-7}/\text{deg C}$ .

In similar manner, an optically clear, glass blank, 1 inch in diameter and 6 inches in length, was produced from a glass having a composition of 5% by weight,  $\text{Sb}_2\text{O}_3$ , and 95% by weight,  $\text{SiO}_2$ . In this case, the  $\text{SiCl}_4$  was maintained in a container at a temperature of 35°C. while  $\text{SbCl}_3$  was maintained, in a separate container, at a temperature of 80°C. Dry oxygen was used as the carrier gas in each case. It was bubbled through the  $\text{SiCl}_4$  container at a rate of 6500 cc./min. and through the  $\text{SbCl}_3$  container at a rate

of 12,000 cc./min. to provide a vapour pick-up of desired magnitude from each container. The separate gas-vapour streams were combined and passed through a combustion burner in which a gas-oxygen mixture was provided from a gas stream flowing at 4900 cc./min. and an oxygen stream flowing at 2700 cc./min. The porous body, produced by collecting the soot from the oxides formed in the burner flame, was introduced into a furnace operating at 1300°C. in the manner described above. An optically clear glass body resulted which, when chemically analyzed, exhibited a composition of 95.6% by weight,  $\text{SiO}_2$ , and 4.4% by weight,  $\text{Sb}_2\text{O}_3$ .

In Tables I and II data for several additional glasses which are Examples of glasses according to the invention are given. The first column in each Table identifies the vaporizable raw materials employed, while the second column indicates the respective temperatures at which these materials were maintained for vapour pick-up. In the Example of Table I, the raw materials were maintained in separate containers and the third column of that Table shows the respective rates of flow of oxygen carrier gas through each container in terms of cc./min.  $\times 10^4$ . In Table II, a mixture of the raw materials was employed and the third column in this Table shows the composition of the mixture in weight percent. In each instance, a porous body was produced and the fourth column of each Table states the temperature, in degrees C., at which this body was thermally vitrified to a glass. Finally, the oxide system and the analyzed composition of each glass produced, in percent by weight on an oxide basis, is shown for each Example.

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TABLE I

| Raw Materials                        | Temp., °C. | O <sub>2</sub> Rates | Temp., °C. Sinter | Oxide System                                     | Analyzed Comp. Wt. % |
|--------------------------------------|------------|----------------------|-------------------|--|----------------------|
| SiCl <sub>4</sub> /SbCl <sub>3</sub> | 35/80      | 0.3/1.5              | 1400              | SiO <sub>2</sub> /Sb <sub>2</sub> O <sub>3</sub> | 79.8/20.2            |
| SiCl <sub>4</sub> /SbCl <sub>3</sub> | 35/80      | 0.075/1.63           | 1280              | SiO <sub>2</sub> /Sb <sub>2</sub> O <sub>3</sub> | 49.1/50.9            |
| SiCl <sub>4</sub> /SbCl <sub>3</sub> | 35/80      | 0.65/1.2             | 1300              | SiO <sub>2</sub> /Sb <sub>2</sub> O <sub>3</sub> | 95.62/4.38           |
| SiCl <sub>4</sub> /SbCl <sub>3</sub> | 35/80      | 1.09/0.75            | 1400              | SiO <sub>2</sub> /Sb <sub>2</sub> O <sub>3</sub> | 97.73/2.27           |
| SiCl <sub>4</sub> /SbCl <sub>3</sub> | 35/80      | 0.4/1.2              | 1350              | SiO <sub>2</sub> /Sb <sub>2</sub> O <sub>3</sub> | 91.5/8.5             |

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TABLE II

| Raw Materials                        | Temp., °C. | Mixture Composition | Temp., °C. Sinter | Oxide System                                    | Analyzed Comp. Wt. % |
|--------------------------------------|------------|---------------------|-------------------|---|----------------------|
| SiCl <sub>4</sub> /PCl <sub>5</sub>  | 35/35      | 22.37/77.63         | 1300              | SiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> | 62.1/37.9            |
| SiCl <sub>4</sub> /PCl <sub>5</sub>  | 35/35      | 19.33/60.67         | 1300              | SiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> | 52.6/47.4            |
| SiCl <sub>4</sub> /PCl <sub>5</sub>  | 35/35      | 77.94/22.06         | 1440              | SiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> | 77.5/22.5            |
| SiCl <sub>4</sub> /PCl <sub>5</sub>  | 35/35      | 87.5/12.5           | 1450              | SiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> | 85.8/14.2            |
| SiCl <sub>4</sub> /PCl <sub>5</sub>  | 35/35      | 6.55/93.45          | 1350              | SiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> | 47.0/53.0            |
| GeCl <sub>4</sub> /TiCl <sub>4</sub> | 35/35      | 13.31/86.69         | 1300              | GeO <sub>2</sub> /TiO <sub>2</sub>              | 67.5/32.5            |
| GeCl <sub>4</sub> /TiCl <sub>4</sub> | 35/35      | 57.6/42.3           | 1300              | GeO <sub>2</sub> /TiO <sub>2</sub>              | 95.19/4.81           |
| GeCl <sub>4</sub> /TiCl <sub>4</sub> | 35/35      | 73.11/26.89         | 1300              | GeO <sub>2</sub> /TiO <sub>2</sub>              | 97.27/2.63           |
| GeCl <sub>4</sub> /TiCl <sub>4</sub> | 35/35      | 64.57/35.42         | 1400              | GeO <sub>2</sub> /TiO <sub>2</sub>              | 95.65/4.35           |
| GeCl <sub>4</sub> /TiCl <sub>4</sub> | 35/35      | 84.46/15.53         | 1200              | GeO <sub>2</sub> /TiO <sub>2</sub>              | 98.56/1.44           |
| TiCl <sub>4</sub> /PCl <sub>5</sub>  | 35/35      | 95.8/4.2            | 1360              | TiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> | 60.4/39.6            |
| TiCl <sub>4</sub> /PCl <sub>5</sub>  | 39/35      | 90.6/9.4            | 1430              | TiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> | 64.8/35.2            |
| TiCl <sub>4</sub> /PCl <sub>5</sub>  | 35/35      | 73.9/26.1           | 1430              | TiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub> | 38.9/61.1            |

FIGURE 3 is a graphical illustration corresponding to FIGURE 1. The refractive index ( $n_d$ ) is plotted along the vertical axis, while glass composition is plotted along the horizontal axis. Each line represents a different binary glass system with the numerical values on the horizontal axis showing the percent, by weight, of the second component of the system. The weight of the first component, of course, is 100 minus the weight of the second component. The symbols in each case represent a glass composition actually melted and measured. It is readily apparent that the present invention not only provides a wide variety of new glass systems that can be produced by flame hydrolysis, but furthermore provides a variety of glass systems that are particularly useful because of their variable refractive indices.

By way of further illustrating the unusual and unexpected results achieved by the invention, reference is made to a series of experiments in which oxide mixtures were produced by different flame hydrolysis procedures. In each case, an identical mixture of  $\text{GeCl}_4$  and  $\text{SiCl}_4$  vapours was introduced into the flame of a combustion burner. The mixture, composed of 16.21% by weight  $\text{GeCl}_4$  and 83.79% by weight  $\text{SiCl}_4$ , was entrained by passing oxygen through the  $\text{GeCl}_4$ - $\text{SiCl}_4$  mixture, in a constant level container, at 35°C.

Initially, the oxides produced in the flame were deposited on a support table rotating within a furnace chamber maintained within the temperature range conventionally used for fused silica glass production by direct vitrification. When the resulting boule was removed after a few hours of deposition and analyzed, it was found to be almost pure  $\text{SiO}_2$ .

In an effort to hold the  $\text{GeO}_2$  in the silica glass, the deposition and vitrification chamber was maintained at a temperature of approximately 1690°C. Again the mixed oxides were produced under essentially identical conditions, and deposited on the rotating support for a period of 3½ hours to form a glass boule. Glass quality was very poor in an optical sense. The oxides vitrified, but tended to form vertical columns with boundaries that distorted light transmission. This is a condition known in the art as "elker teeth". Furthermore, chemical analysis showed 0.026% by weight  $\text{GeO}_2$  rather than the theoretical 6.76% by weight  $\text{GeO}_2$ .

Thereafter, the oxides formed were collected outside the furnace chamber in the particulate form known as "soot". When this soot was analyzed a content of 4.70% by weight  $\text{GeO}_2$  was found. A sample of soot was then collected as a shaped body and introduced, during a period of ½ hour, into a furnace having a maximum temperature of 1550°C, to gradient fire the body. The

body was removed and found to be a completely vitrified glass body having good optical quality and an analytical content of 4.70% by weight  $\text{GeO}_2$ .

The precise reason why the invention works is not readily apparent. Differential volatility may be advanced as an explanation. However, vapour pressure data do not fully support this. This may be seen from the following Table which sets forth the approximate boiling point, and the approximate temperature corresponding to a vapour pressure of 100 mm. Hg for each oxide (except  $\text{TeO}_2$ , where boiling point data are not available).

| Oxide                   | Table III          |                      |
|-------------------------|--------------------|----------------------|
|                         | Boiling point (°C) | 100mm. pressure (°C) |
| $\text{GeO}_2$          | 1700               | 1550                 |
| $\text{P}_2\text{O}_5$  | 600                | 500                  |
| $\text{TeO}_2$          | —                  | 1100                 |
| $\text{Sb}_2\text{O}_3$ | 1570               | 1000                 |

It will be appreciated that a vapour pressure of 100 mm. Hg is sufficiently high that substantial volatilisation should also be expected at a temperature corresponding to that pressure. Nevertheless, this expected loss is not encountered when, for example,  $\text{GeO}_2$ - $\text{SiO}_2$  glasses are consolidated at a temperature corresponding to such vapour pressure.

It is believed that volatilisation does tend to occur in the single oxide type glass, e.g., a pure  $\text{GeO}_2$  or  $\text{Sb}_2\text{O}_3$  glass. Furthermore, it may occur in a mixed glass such as  $\text{GeO}_2$ - $\text{Sb}_2\text{O}_3$  glass. Hence, it is necessary to minimize both the collection and the consolidation temperatures to avoid material loss. In particular, at temperatures greater than 200 deg C. above the minimum consolidation temperature, the degree of loss becomes so great that collection and/or consolidation are impractical.

Contrary to this, however, it is believed that volatilisation loss, to a substantial extent at least, does not occur in a binary or more complex system involving a metal oxide other than the four statedly volatile oxides used according to the present invention, despite the fact that vapour pressure is relatively high at the consolidation temperature. It is believed that an interaction or interbonding occurs that limits volatilisation. Thus, the  $\text{GeO}_2$ - $\text{SiO}_2$  glass may be consolidated at 1550°C. without the expected loss. However, as the temperature is further increased this bond weakens and the effect is lost rapidly, with the result that substantially complete loss of  $\text{GeO}_2$  can readily occur below 1700°C.

#### WHAT WE CLAIM IS:—

1. A fused oxide glass, being either a tellurate glass or a glass comprising at least one oxide selected from  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ , and



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- Sb<sub>2</sub>O<sub>3</sub>, comprising GeO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>3</sub>, or TeO<sub>2</sub>, in an amount in excess of 0.1% by weight, and having a cation impurity level, as hereinbefore defined, not exceeding 10 ppm, by weight.
- 5 2. A glass as claimed in Claim 1, which consists of a single oxide.
3. A glass as claimed in Claim 2, in which the said oxide is GeO<sub>2</sub>.
- 10 4. A glass as claimed in Claim 1, which comprises at least one additional compatible oxide.
5. A glass as claimed in Claim 4, comprising GeO<sub>2</sub>-SiO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub>, GeO<sub>2</sub>-TiO<sub>2</sub>, or P<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>.
- 15 6. A glass as claimed in Claim 1, substantially as herein described.
7. A glass as claimed in Claim 1, substantially as herein described with reference to any one of the Examples.
- 20 8. A method of making a glass as claimed in Claim 1, comprising:
- (a) entraining in a gas stream at least one vaporizable compound, at least one of which may be converted, by flame hydrolysis and decomposition, into GeO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, TeO<sub>2</sub>, or Sb<sub>2</sub>O<sub>3</sub>, in an amount in excess of 0.1% by weight,
- 25 (b) passing the gas stream into the flame of a combustion burner,
- (c) collecting the resulting oxide in particulate form,
- (d) shaping the oxide particles as a porous body,
- (e) heating the said shaped body to consolidate the porous body to a non-porous glass body, and
- 35 (f) maintaining the particle temperature at not more than 1600°C, and at not more than 200 deg C above the minimum consolidation temperature of the porous body, during the deposition and consolidation steps.
9. A method as claimed in Claim 8, substantially as herein described.
- 45 10. A method as claimed in Claim 8, substantially as herein described with reference to any one of the Examples.
11. A glass when made by a method as claimed in any of Claims 8 to 10.
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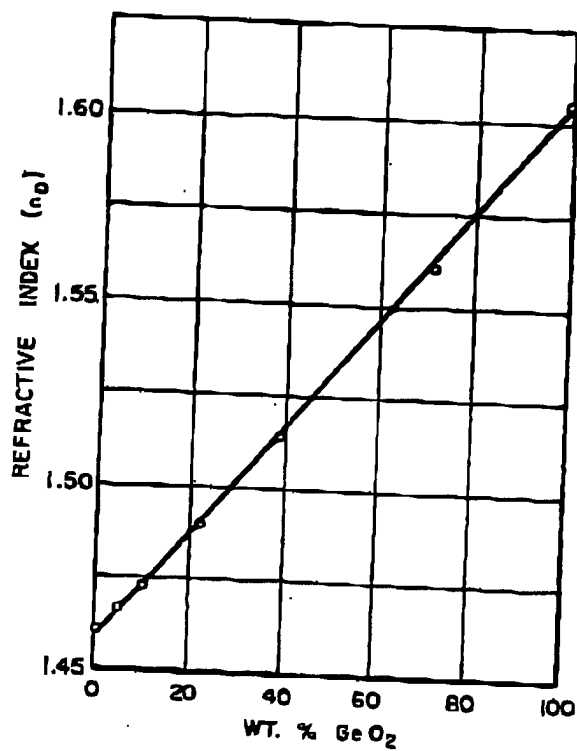
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COMPLETE SPECIFICATION

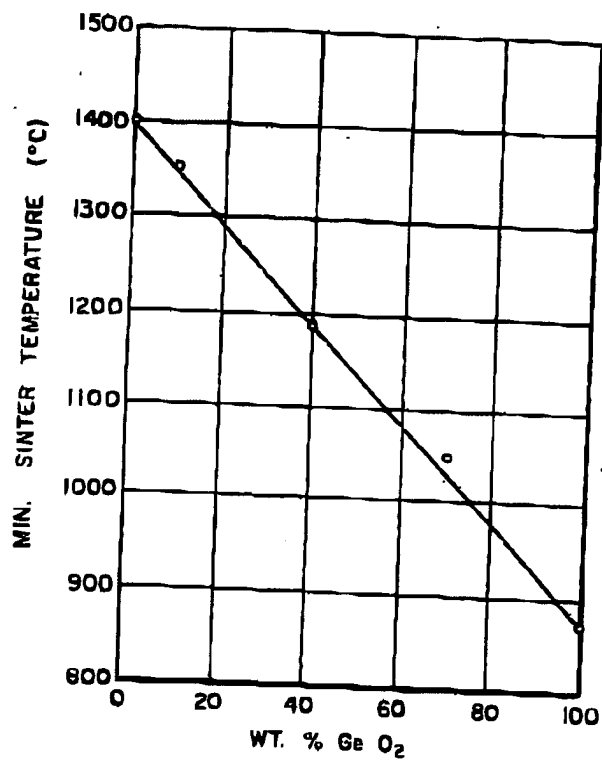
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Sheet 1

*Fig. 1*

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**Fig. 2**

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